Hybrid plasma-catalytic steam reforming of toluene as biomass tar model compound over Ni/Al_2O_3 catalysts

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Abstract

In this study, plasma-catalytic steam reforming of toluene as a biomass tar model compound was carried out in a coaxial dielectric barrier discharge (DBD) plasma reactor. The effect of Ni/Al_2O_3 catalysts with different nickel loadings (5-20 wt. %) on the plasma-catalytic gas cleaning process was evaluated in terms of toluene conversion, gas yield, by-products formation and energy efficiency of the plasma-catalytic process. Compared to the plasma reaction without a catalyst, the combination of DBD with the Ni/Al_2O_3 catalysts significantly enhanced the toluene conversion, hydrogen yield and energy efficiency of the plasma process, whilst significantly reduced the production of organic by-products. Increasing Ni loading of the catalyst improved the performance of the plasma-catalytic processing of toluene, with the highest toluene conversion of 52 % and energy efficiency of 2.6 g/kWh when placing the 20 wt.% Ni/Al_2O_3 catalyst in the plasma. The possible reaction pathways in the plasma-catalytic process were proposed through the combined analysis of both gas and liquid products.

Keywords: plasma-catalysis; non-thermal plasma; dielectric barrier discharge; biomass gasification; tar removal

1. Introduction

Biomass has great potential to make a major contribution to the low carbon economy and reaching COP21 targets. Biomass gasification has been regarded as a key thermochemical route for the production of a higher value syngas from a renewable and CO_2-neutral source [1]. The product gas or synthesis gas (a mixture of H_2 and CO) produced from biomass gasification can be used for generating electricity and heat by direct combustion in internal engines, while high quality synthesis gas can also be used as an important chemical feedstock for the synthesis of a variety of valuable fuels and chemicals. Clearly, biomass can make a significant contribution to all three key energy sectors: transport, heat and electricity [2, 3].

However, one of the major challenges in the biomass gasification process is contamination of the product syngas with tar, which is a complex mixture of condensable hydrocarbons with molecular weight higher than benzene, some of which are carcinogenic. The content of tar in the produced syngas from biomass gasification varies from 1 g/m^3 up to 100 g/m^3, depending on the operating conditions of the gasification process [4] . The production of tars in biomass gasification process leads to major process and syngas end-use problems, including tar blockages, plugging and corrosion in downstream fuel lines, filters, engine nozzles and turbines, and has been a major barrier for the development and deployment of biomass gasification process [3, 4]. Considerable efforts have been focused on the removal of tars in product gas from biomass gasification using different processes, including thermal cracking [5, 6], physical separation [7] and catalytic reforming [3, 8-10]. Thermal cracking of tars requires very high reaction temperature (>800 ^oC) and thus cause a high energy input. Physical separation of tars could reduce the efficiency of the overall process and has great potential to cause secondary pollution. Along with the requirement for high temperature in thermal catalytic reforming process, rapid deactivation of catalysts due to coke deposition is the major challenge in thermal-catalytic reforming process.

The least researched, yet predicted to be the most attractive and effective, is the plasma gas cleaning process. Non-thermal plasma has been demonstrated as an effective solution for the removal of organic gas pollutants (e.g. volatile organic compounds VOCs) and synthesis of chemicals and fuels [11]. In non-thermal plasmas, the produced electrons are highly energetic (1-10 eV) and can break most chemical bounds of inert molecules, producing reactive species including free radicals, excited atoms, ions and molecules for a variety of chemical reactions. In addition, high reaction and fast reaching of a steady state in a plasma process allows rapid switch on and off the plasma process compared to other thermal processes, which significantly enhance the overall energy efficiency and provides a promising route for plasma process supplied by renewable energy (e.g. wind power or solar power) to act as an efficient chemical energy storage localized or distributed system at peak grid times [12, 13].

A more effective use of plasma is to integrate plasma process with heterogeneous catalysis, combining the advantages of fast and low temperature reaction by non-thermal plasmas and selective synthesis from catalysis. The combined plasma-catalytic process has great potential to produce a synergy, which can low the activation energy of catalysts and enhance the conversion of reactants, the selectivity and yield of desirable products, and the efficiency of the plasma process [11, 14]. This novel hybrid process has attracted significant interest for gas clean-up, methane activation, CO_2 conversion, synthesis of carbon nanomaterials and catalysts [15]. However, very limited work has been focused on the use of non-thermal plasma for the removal of tars from the gasification of biomass or waste. To the best of our knowledge, no work has been dedicated to the investigation of hybrid plasma-catalytic process for the removal of tars from biomass gasification. So far, a range of catalysts have been evaluated in thermal-catalytic reforming of tars at high temperatures, such as calcined rocks, clay minerals, ferrous metal oxides, activated alumina and supported-metal catalysts (e.g. nickel, cobalt and other noble metals) [16]. Nickel catalysts mainly supported on

alumina, have been extensively investigated for thermal catalytic tar reforming because of its high initial activity, abundance and low cost. However, catalyst deactivation due to coke deposition remains a major challenge in catalytic reforming of tars. Our previous works showed that the coupling of plasma with Ni/Al_2O_3 catalysts can significantly reduce carbon deposition in plasma-catalytic reforming of biogas compared to thermal catalytic reactions [17]. However, it is not clear how a catalyst (e.g. Ni/Al_2O_3) present in the plasma process affects the reforming of tars or a tar model compound at low temperatures. Furthermore, previous studies mainly investigated the effect of different operating parameters on the performance of the plasma tar removal process [18, 19], whereas few analyzed the by-products and intermediates in the plasma reforming of tar to better understand the underlying reaction pathways and mechanisms in the plasma process. In addition, a detailed understanding of the underlying reaction pathways and mechanisms in the plasma processing of tars is still missing. It is of primary importance to analyze both the gas and condensed liquid products in the plasma-catalytic steam reforming process to get new insights into the reaction pathways, which would provide valuable information for the further optimization of the plasma-catalytic process.

The present study aimed to demonstrate the effectiveness of the hybrid plasma-catalytic process for the removal of a tar model compound and provide an insight of toluene destruction pathways in the plasma-catalytic process. In this work, an in-plasma catalysis (IPC) system based on a coaxial dielectric barrier discharge (DBD) reactor was developed for the steam reforming of toluene, a typical model tar compound representing a major stable aromatic product in the tars formed in high temperature biomass gasification processes. The effect of $Ni/\gamma\text{-}Al_2O_3$ catalysts with different Ni loadings (5 to 20 wt.%) on the plasma-catalytic removal of toluene was investigated in terms of toluene conversion, energy efficiency of the plasma-catalytic process and the distribution of gas products. The plasma

steam reforming process without a catalyst was also carried out for comparison. Moreover, the possible reaction pathways involved in the plasma reactions were proposed and discussed through combined quantitative and qualitative analysis of gas and liquid products.

2. Experimental

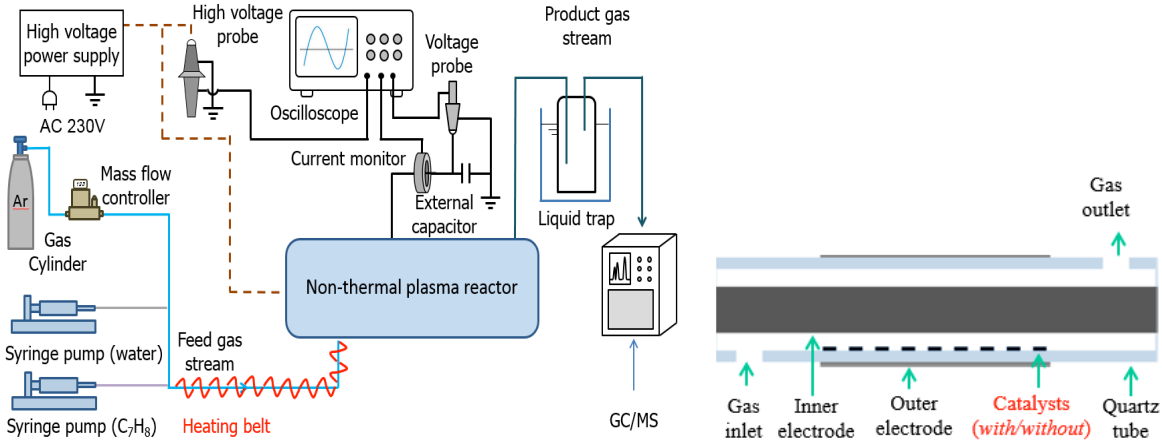
2.1. Catalyst preparation

The Ni/γ-Al_2O_3 catalysts with different Ni loadings (5, 10 and 20 wt. %) were prepared by the wetness impregnation method. The appropriate weight of γ-Al_2O_3 (1 mm diameter beads) was added to the metal precursor solution and impregnated for 12 hours. The above solution was dried at 100 ^oC until most of water was evaporated. The obtained samples were heated at 100 ^oC for 24 h, followed by the calcination at 750 ^oC for 3 h.

2.2. Experimental setup

The experiments were carried out in a coaxial DBD reactor (Fig.1). A 100 mm-long stainless steel (SS) mesh was wrapped over a quartz tube with an inner diameter of 18 mm and outer diameter of 21 mm. A SS rod with a diameter of 14 mm was used as an inner electrode and placed in the axis of the quartz tube. As a result, the length of the discharge region was 100 mm with a discharge gap of 2 mm. The inner electrode was connected to a high voltage output and the outer electrode was grounded via an external capacitor C_{ext} (0.47 μF). The DBD reactor was connected to an AC high voltage power supply with a maximum peak voltage of 30 kV and a frequency of 5-20 kHz. In this work, the frequency was fixed at 9 kHz. The applied voltage was measured by a high voltage probe (Testec, TT-HVP 15 HF), while the voltage on the external capacitor was recorded by a voltage probe (Tektronix P5100) to obtain the charge generated in the discharge. All the electrical signals were recorded by a

4-channel digital oscilloscope (Tektronix MDO 3024). The Q-U Lissajous method was used to determine the discharge power (P) of the DBD reactor. A homemade online power measurement system was used to monitor and control the discharge power in real time [20].



(a) (b)

Fig.1 Schematic diagram of the (a) experimental setup; (b) DBD reactor

A total of 0.5 g of Ni/γ-Al_2O_3 catalyst was packed into the plasma region along the bottom of the quartz tube, partially filling the discharge gap and held by quartz wood. This partial packing method has been shown to effectively enhance the interactions between the plasma and catalyst in a DBD reactor and consequently promoted the plasma-catalytic chemical reactions in our previous studies [21]. Before the reaction, the catalysts were reduced in a H_2 plasma at a discharge power of 60 W and a flow rate of 50 mL/min for 1 h in the same DBD reactor. Then, argon was used as a carrier gas with a flow rate of 150 mL/min. Toluene (C_7H_8, purity >= 99%, Aldrich) solution and deionized water were injected into the preheated pipe by high-resolution syringe pumps (KDS Legato, 100) at a flow rate of 0.2 ml/h and 0.6 mL/h, respectively. The steam-to-carbon molar ratio (S/C ratio) was fixed at 2.5 throughout the experiment. The mixed stream was heated to 160 ^{o}C in a copper pipe with an inner diameter

of 4 mm (40 cm in length) controlled a temperature controller system, to produce a steady-state vapour before flowing into the plasma reactor.

2.3. Methods of analysis and the definition of parameters

The gas products were analyzed by a two-channel gas chromatography (Shimadzu, GC-2014) equipped with a flame ionization detector (FID) for the measurement of C_1-C_4 hydrocarbons and a thermal conductivity detector (TCD) for the analysis of H_2, CO, CO_2 and CH_4. During the reaction, an ice trap was placed at the exit of the DBD reactor to condense liquid products. The collected liquid samples were analyzed by a gas chromatography – mass spectrometry (GC-MS, Agilent GC 7820 A, MSD) and qualitatively identified using the mass spectral library from National Institutes for Standards and Technology (NIST) [22]. All the measurements were performed after running the plasma reaction for around 30 mins when the plasma reaction reached a steady-state.

In the plasma reforming reaction, the conversion of toluene $X_{C_7H_8}$, was calculated as the moles of carbon in the carbon-containing gas products (CO_2, C_2H_2, C_2H_4, C_2H_6 and C_3H_8) to the carbon in the input toluene:

$$X_{C_7H_8}(\%) = \frac{\text{Moles of carbon in the produced gas}}{\text{Moles of carbon in the feed}} \times 100 \quad (2)$$

The yield of the products was defined as follows:

$$Y_{H_2}(\%) = \frac{H_2 \text{ produced}(\text{mol/s})}{4 \times C_7H_8 \text{ input } (\text{mol/s}) + H_2O \text{ input}(\text{mol/s})} \times 100 \quad (3)$$

$$Y_{CO_2}(\%) = \frac{CO_2 \text{ produced } (\text{mol/s})}{7 \times C_7H_8 \text{ input } (\text{mol/s})} \times 100 \quad (4)$$

$$Y_{C_xH_y}(\%) = \frac{x \times C_xH_y \text{ produced } (\text{mol/s})}{7 \times C_7H_8 \text{ input } (\text{mol/s})} \times 100 \quad (5)$$

The energy efficiency (E) of the plasma reforming toluene conversion was defined as the mass of converted toluene per unit of discharge power.

$$E(\text{g/kWh}) = \frac{\text{mass of converted } C_7H_8 \text{ (g/h)}}{\text{discharge power (kW)}} \quad (6)$$

3. Results and discussion

3.1. Plasma-catalytic steam reforming of toluene

Plasma steam reforming of toluene was carried out in the DBD reactor with and without the Ni catalysts, as shown in Fig. 2. Compared with the plasma reaction without a catalyst, the presence of the 10 wt.% Ni/γ-Al_2O_3 catalyst in the plasma significantly enhanced the carbon conversion by around 20% (from 39.5 % to 47.1%), whilst the energy efficiency of the process was increased by 18.0 %. Tao et al reported similar findings in a plasma-catalytic steam reforming of high content toluene (~200 g/Nm^3) over a 5 wt.% Ni/SiO_2 catalyst in a DC plasma reactor [23]. However, extra thermal heating (at 773 K) was used to heat the plasma-catalytic process in their experiments. Therefore, it was extremely difficult to identify whether the effect of the Ni/SiO_2 catalyst on the enhanced toluene conversion was driven by the plasma or thermal heating or both [23].

In this study, the Ni catalysts were placed along the bottom of the discharge region in the DBD reactor, while the plasma-catalytic steam reforming reaction was carried out at low temperatures (<200 ^oC) without any external heating. Therefore, heating effect from the plasma on the catalyst activation and plasma-catalytic reaction was negligible. As shown in Fig. 3, this partial packing method could still generate a strong filamentary discharge in the

DBD reactor due to the presence of large void fraction in the discharge gap, resulted in strong physical and chemical interactions between the discharge and Ni catalysts [21]. Compared to the plasma reaction without packing, the shape of the Lissajous figure was almost same when the catalysts were partially packed into the discharge region (Fig. 4). Moreover, when a catalyst is placed in the discharge, polarisation of the catalyst leads to the charge accumulation on the catalyst surface, increasing the local or average electrical field and therefore the number of energetic electrons and reactive species, characterized by the formation of intensified microdischarges around the contact points between the catalyst pellets and those between the catalyst pellet and quartz wall [24, 25]. Previous studies demonstrated that placing a 10 wt.% Ni/γ-Al_2O_3 along the bottom of a DBD reactor enhanced the intensity of current pulses in the plasma-catalytic dry reforming of CH_4 [21], while the mean electric field and mean electron energy of the DBD were enhanced by 9-11% when $BaTiO_3$ and TiO_2 photocatalysts were partially packed in the DBD reactor in the plasma-catalytic conversion of CO_2 [14]. These physical effects have been shown to enhance the conversion of reactants in plasma-catalytic chemical reactions. Similar phenomenon was also observed in Fig. 2. Clearly, in this study, the enhanced toluene conversion and energy efficiency in the plasma-catalytic steam reforming of toluene can be partly attributed to the physical effects induced by the presence of the Ni catalyst pellets in the plasma.

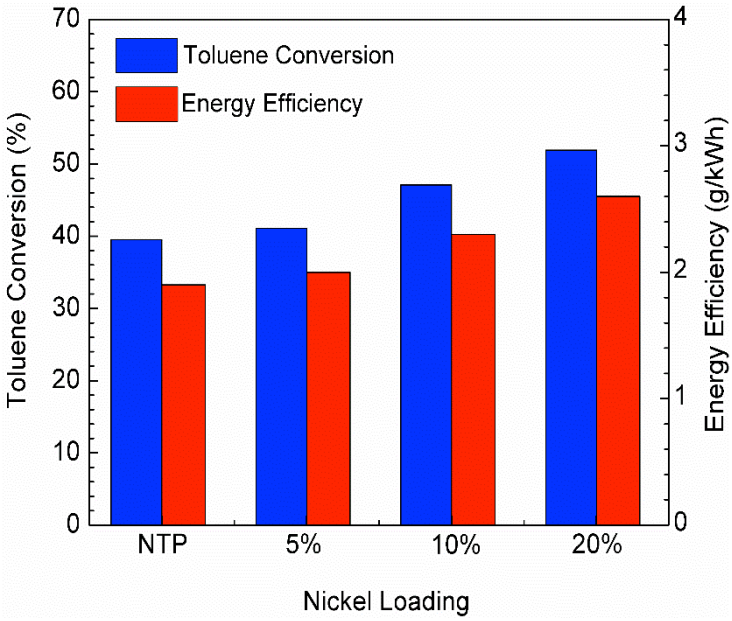
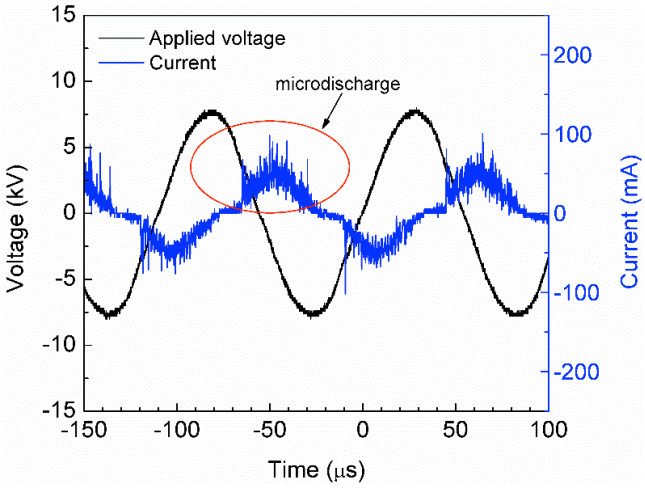
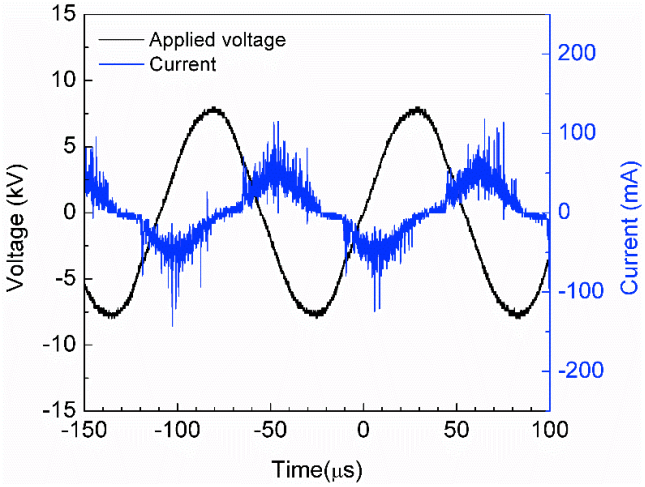


Fig. 2. Toluene conversion and energy efficiency of the plasma process with and without catalysts (toluene concentrate: 17.7 g/Nm^3, discharge power: 35 W, S/C ratio: 2.5, catalyst: 10 wt.% Ni/γ-Al_2O_3)



(a)



(b)

Fig. 3. Electrical signals of the DBD (a) without packing; (b) with 10 wt.% Ni/γ-Al_2O_3 catalyst

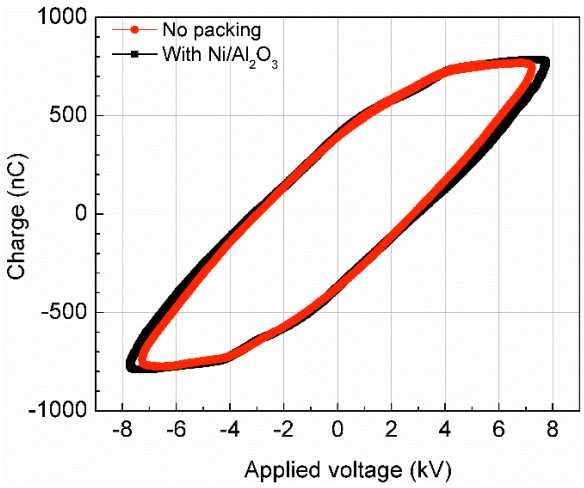


Fig. 4. Lissajous figures of DBD plasma with and without 10 wt.% Ni/γ-Al_2O_3 catalyst at a constant discharge power of 35 W.

In addition, increasing the Ni loading from 5% to 20% increased the conversion of toluene and energy efficiency of the plasma-catalytic process, as shown in Fig. 2. For example, the combination of the DBD with the 20 wt.% Ni/γ-Al_2O_3 catalyst showed the highest toluene conversion of ~51.9 % and energy efficiency of 2.6 g/kWh. In the plasma-catalytic reforming

reaction at low temperatures, increasing the Ni loading over γ-Al_2O_3 could effectively enhance the catalyst activity owing to the formation of more active Ni sites on the catalyst surface. Aziznia et al also showed that higher conversions of CO_2 and CH_4 were obtained in the low temperature plasma-catalytic dry reforming of CH_4 when a 20 wt.% Ni/γ-Al_2O_3 catalyst was placed in a corona discharge compared with Ni/γ-Al_2O_3 catalysts with a lower Ni loading (5 wt.% and 10 wt.%) [26]. Similar phenomenon was also observed in thermal catalytic chemical reactions. Wang reported that the removal efficiency of tar and hydrogen production increased with increasing Ni loading from 5 wt.% to 20 wt.% [27]. Aziz et al investigated the effect of Ni loading (1-10 wt. %) on CO_2 methanation over Ni/mesoporous silica nanoparticles (MSN) catalysts at different reaction temperatures [28]. They found that increasing the Ni loading enhanced the catalytic activity for CO_2 methanation at low temperatures (< 623 K). However, the 10 wt. % Ni/MSN catalyst showed a similar activity as the 5 wt. % Ni/MSN catalyst in CO_2 methanation at high temperatures (>673 K). Similarly, Liu et at reported that there was an optimum Ni loading of 10 wt.% of activated carbon (AC) supported Ni catalysts in thermal catalytic steam reforming of toluene at 200 ^oC. They found that further increasing the Ni loading to 15 wt.% increased the nickel particle size and lowered the nickel particle dispersion on the catalyst surface, resulted in the aggregation of Ni particles and increased carbon deposition, and consequently decreased the conversion of toluene. Compared to relatively high temperature thermal catalytic reactions, placing supported metal catalysts in low temperature plasma process can effectively reduce the metal particle size and enhance the metal dispersion on the catalyst surface due to low temperature effect [29]. In this experiment, low temperature plasma reaction is believed to avoid the aggregation of Ni particles on the catalyst surface but increase the catalytic activity for toluene conversion when increasing the Ni loading from 5 wt. % to 20 wt.%. In addition, the presence of conductive Ni species on the catalyst also contribute to the expansion of the

plasma over the catalyst surface, which may be favourable to the expansion of discharge volume and intensity in the DBD-catalytic process [30].

These results clearly demonstrated that the catalytic effect (e.g. catalyst activity) also plays an important role in enhancing the conversion of toluene and efficiency of the plasma-catalytic process besides the physical effects. In the hybrid plasma-catalytic process, the adsorption of reactants on the catalyst surface could be enhanced [24], which would increase the retention time of toluene and its intermediates in the plasma and therefore improve the collision probability between these pollutants and chemically reactive species, leading to a higher toluene conversion in the plasma-catalytic process.

3.2. Gaseous products

H_2, CO_2 and CH_4 were found as the main gas products in the plasma steam reforming of toluene with and without the Ni catalyst. A small amount of hydrocarbons (C_2H_2, C_2H_4, C_2H_6, C_3H_8 and C_4H_{10}) were also detected. Clearly, the presence of the Ni catalysts in the DBD reactor enhanced the production of H_2 and CO_2, as shown in Fig. 5. Increasing the Ni loading from 5 to 20 wt.% steadily increased the yield of H_2 and CO_2 by 15% and 16%, respectively. It is worth to note that no CO was detected in the gas products. The occurrence of water gas shift reaction (R1) could be the major reason to inhibit the generation of CO in the reforming of toluene in the DBD. Moreover, the presence of reactive oxide species (e.g. OH, O radicals) through the dissociation of water by energetic electrons and metastable argon might be able to further oxidize CO (R4 and R5), toluene and its intermediates into CO_2. This plasma reaction might be considered as an attractive hydrogen production process without CO formation suitable for fuel cell applications.

$$H_2O + CO \rightarrow CO_2 + H_2 \quad \text{(R1)}$$

$$H_2O + e \rightarrow H^- + OH \quad \text{(R2)}$$

$$H_2O + e \rightarrow 2H + O^- \quad \text{(R3)}$$

$$OH + CO \rightarrow CO_2 + H \quad \text{(R4)}$$

$$O + CO \rightarrow CO_2 \quad \text{(R5)}$$

As shown in Fig. 5, the yield of CH_4 was nearly constant (~10%) when changing the Ni loading, whereas the yield of C_3-C_4 hydrocarbons (less than 1.6 %) increased by increasing the Ni content. Compared to the plasma reaction with no catalyst, placing the 5 wt.% Ni/γ-Al_2O_3 catalyst in the DBD reactor almost did not change the production of C_2H_2 and C_2H_6. However, increasing Ni content from 5 to 20 wt. % enhanced the yield of C_2H_2 and C_2H_6. The highest C_2H_2 yield of 5.2% was achieved when the 20 wt.% Ni/γ-Al_2O_3 catalyst was placed in the plasma steam reforming of toluene.

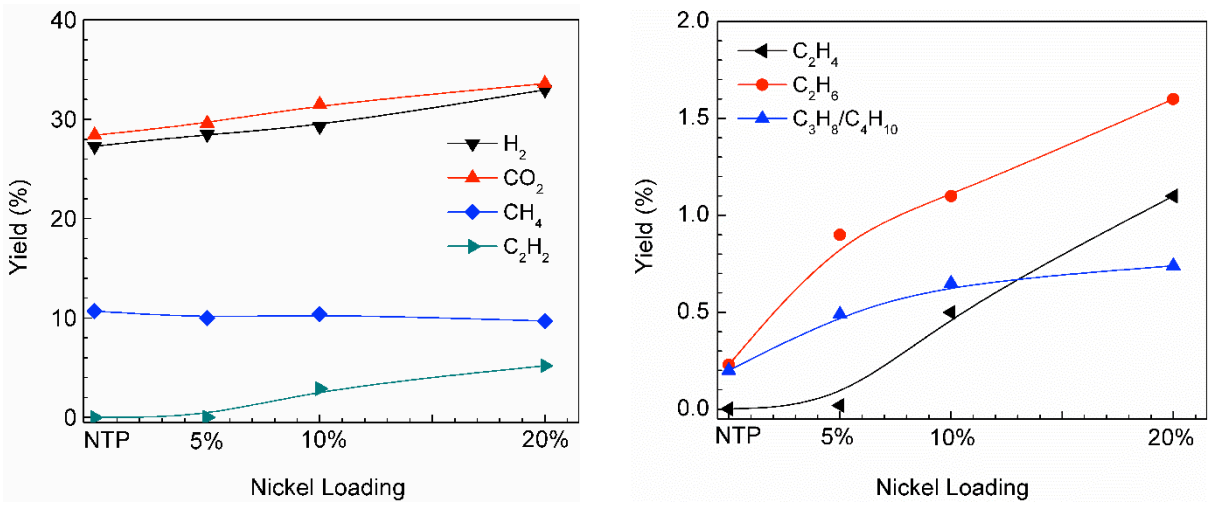


Fig. 5. The effect of Ni loading on the yield of gaseous products (toluene concentrate: 17.7 g/Nm^3, discharge power: 35 W, S/C: 2.5)

3.3. Formation of condensed by-products

Fig. 6 shows the GC-MS chromatogram of condensed by-products collected in the plasma steam reforming of toluene with and without the catalyst. In the plasma reaction without a catalyst, 11 types of organic by-products were detected, including major compounds such as benzene, phenol and (butoxymethyl)-benzene. Additionally, aliphatic compounds such as methyl ester, diol, octadecadienoic acid and the linear compounds 5, 7-Dodecadiyn-1, 12-diol were also detected, which could be generated from the cleavage of toluene ring, and the recombination and hydrogenation of the resulting fragments of intermediates. The presence of the 5 wt.% Ni/γ-Al_2O_3 catalyst in the plasma process significantly inhibited the formation of organic by-products. As shown in Fig. 6(b), only six types of condensed compounds were detected, among which phenol, 2,4-Hexadien-1-ol and (butoxymethyl)-benzene were identified as the major organic by-products. It is worth noting that the amount of phenol and (butoxymethyl)-benzene formed in the plasma-catalytic reforming reaction was several orders of magnitude lower than those generated in the plasma reaction without the Ni catalyst. These results clearly demonstrated that the coupling of the DBD and the Ni/γ-Al_2O_3 catalyst promoted the conversion of toluene into gas products (e.g. H_2), whilst significantly minimized the formation of undesirable organic by-products (Fig. 6).

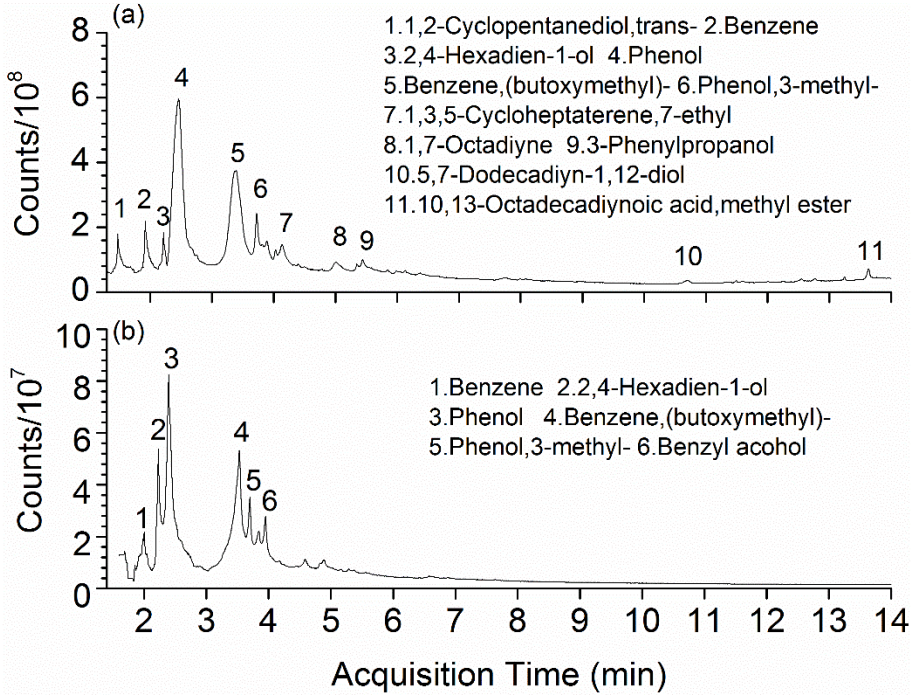


Fig. 6. GC-MS chromatogram of condensed by-products collected in the plasma steam reforming of toluene (a) without a catalyst, and (b) with the 5 wt. % Ni/γ-Al_2O_3 catalyst (toluene concentration: 17.7 g/Nm^3, discharge power: 35 W, S/C: 2.5, catalyst: 0.5g)

3.4. Reaction mechanisms and pathways of toluene destruction

The reaction mechanism in the destruction of toluene (50 -500 ppm) as a model VOC in air or nitrogen plasmas without a catalyst has been investigated and proposed in previous studies [31, 32]. However, very limited work has focused on the understanding of the reaction routes in the plasma reforming of toluene as a model tar compound, especially in the presence of a catalyst. Compared to the removal of toluene as a model VOC, the reaction pathways present in the plasma steam reforming of toluene could be different due to the presence of high content toluene and steam. To get new insights into the possible reaction routes in this plasma process, the analysis of both gaseous and condensed liquid by-products were carried out in the plasma reaction with and without the Ni catalyst. It is well known that only gas-phase

reactions are involved in the plasma reforming of toluene without the Ni catalyst. However, placing the Ni catalyst in the DBD makes the reaction more complicated as plasma driven surface reactions occur besides the gas-phase reactions.

The destruction of toluene as a model tar compound in the argon DBD can be initiated through two major reaction routes: (i) direct electron impact dissociation of toluene and (ii) reaction with chemically reactive species including OH and Ar metastable species. The ionization of Ar requires a much higher electron energy (15.76 eV) compared to the excitation of Ar to its metastable states Ar^* (e.g. 11.55 eV). Therefore, in the Ar DBD, Ar is more likely to be excited to its metstable states rather than being ionized [33]. Previous studies have shown that metastable Ar species play an important role in initiating chemical reactions [34]. The presence of steam in the plasma could generate OH radicals from the dissociation of water by electrons and Ar*. The generated OH radicals can oxidize toluene and its intermediates, opening a new reaction route for the conversion of toluene, resulting in the enhanced conversion and energy efficiency of the plasma process [35].

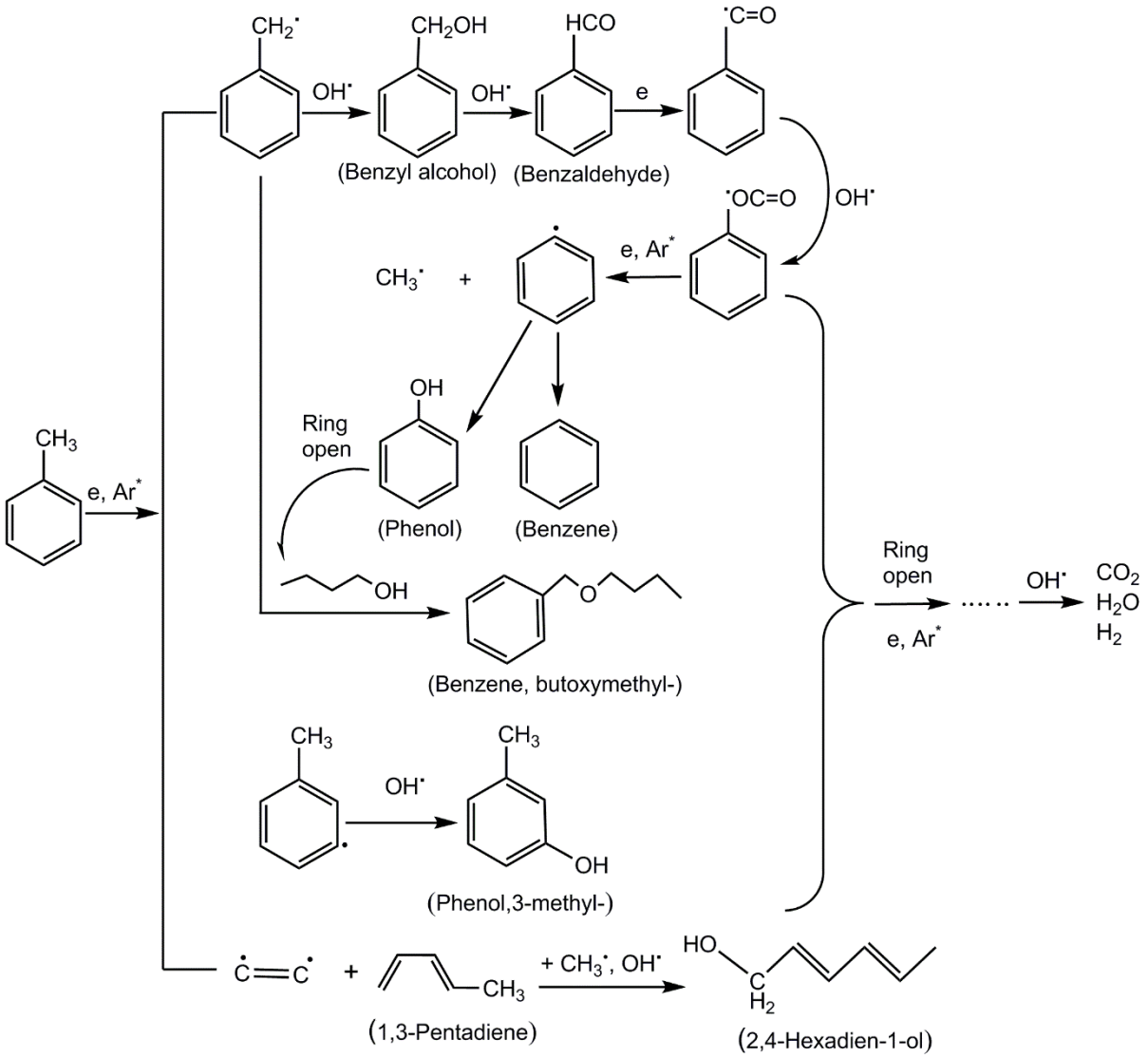
Different bond energies of chemical bonds in toluene determine the reaction pathways involved in the plasma conversion of toluene. The dissociation energy of C-H bond in methyl is 3.7 eV, which is smaller than that of C-H bond in aromatic ring (4.3 eV), C-C bond between aromatic ring and methyl group (4.4 eV), C-C bond (5.0-5.3 eV) and C=C bond in aromatic ring (5.5 eV). Therefore, the primary reaction pathway of toluene decomposition could be the H-abstraction from methyl group by energetic electrons or reactive species such as Ar* and OH [36]. The H-abstraction from the methyl group forms a benzyl radical, which could further react with OH to generate benzyl alcohol. The formed benzyl alcohol can be converted to benzaldehyde, followed by further reactions with electrons and reactive species to form a phenyl radical [37]. In addition, the C-C bond between methyl and aromatic ring

and C-H bond in the aromatic ring can be broken through the reactions with energetic electrons and metastable Ar species, generating phenyl, methyl, and toluene radicals [32]. As shown in Fig. 7(a), the recombination of phenyl with H and OH radicals could produce benzene and phenol, respectively, while adding OH to the aromatic ring of toluene radicals produces 3-methyl phenol, as identified by GC-MS. Moreover, ring opening and cracking of phenol via electron impact dissociation forms butyl alcohol, which then reacts with benzyl to generate benzene, (butoxymethyl). These aromatic intermediates can be further ruptured by electrons and Ar^* species to form ring-opening by-products and then oxidized by OH to end-products such as CO_2 and H_2O.

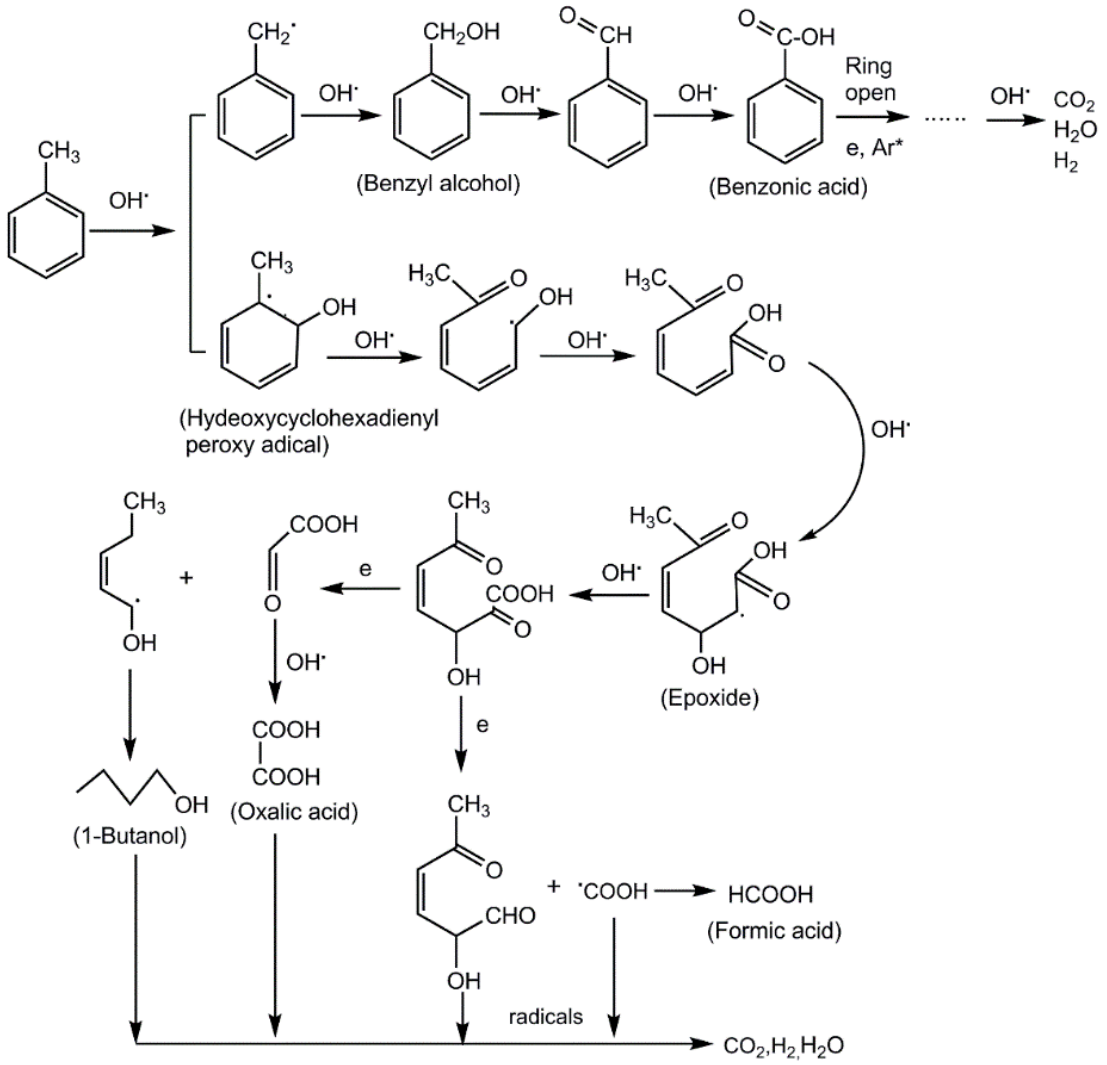
Toluene can also be decomposed by the cleavage of benzene ring through collisions with reactive species, e.g. OH radicals, producing hydroxycyclohexadienyl type peroxy radicals (Fig. 7(b)), which has been confirmed in the previous modeling and experimental studies [37-39]. This reactive compound is unstable and can form a peroxide bridge radical, a precursor for the formation carbonyl and epoxide [39]. The carbonyl reaction route opens the benzene ring of toluene via a stepwise oxidation by OH species to form a relatively stable epoxide, which can be further decomposed by electrons or active species, forming small molecules, such as oxalic acid and acetic acid.

The presence of the Ni catalysts in the plasma steam reforming of toluene enhanced the production of most gas products, whilst significantly reduced the formation of condensed organic by-products. These findings suggest that the combination of the plasma with the Ni catalysts shifted the primary reaction pathways of toluene destruction from the dehydrogenation or oxygenation of methyl group to direct cleavage of toluene ring, which can be evidenced by the enhanced yield of hydrogen and C_2H_2. Previous experimental and theoretical studies showed that acetylene was most likely formed by rupturing the toluene

ring through the collisions with electrons and Ar^* species [40]. Recently, Zhu et al. also reported that high energetic electrons could breakdown toluene ring, forming acetylene and methyl-cyclobutadiene in the plasma decomposition of toluene as a tar surrogate using a rotating gliding arc discharge [41]. In this work, the detected C_5H_6 might be 1, 3-pentadiene, which sequentially reacted with methyl and OH radicals to form linear hydrocarbons such as 2, 4-hexadien-1-ol. In the hybrid plasma-catalytic reforming of toluene, plasma-assisted surface reactions also contributed to the enhanced reaction performance. In our experiment, the Ni catalyst pellets were placed along the button of the quartz tube in the discharge region and can directly interact with the plasma. Partial packing of the Ni catalyst pellets in the DBD still formed predominant micro-discharges across the electrode gap and induced strong interactions between the plasma and Ni catalyst, which is favourable for the plasma induced surface reactions on the surface of the Ni catalyst [21]. In this plasma-catalysis configuration, both toluene and its intermediates formed in the gas phase reactions can be adsorbed on the surface of the Ni catalyst. Short-lived reactive species (e.g. O, OH) initially generated close to or on the catalyst surface can also be involved in the surface reactions. The excited species generated in the plasma might accelerate the adsorption of toluene and intermediates onto the catalyst surface [42]. The residence time of toluene and intermediates in the plasma reaction region could be prolonged due to the catalyst effect. The enhanced adsorption increases the collisions of toluene with energetic species, consequently accelerates the plasma reactions, both in the gas phase and on the catalyst surface. The adsorbed species could also react with oxidative radicals, forming intermediates such as benzoic acid, before finally oxidized to produce end-products such as CO_2 and H_2O.


CH2•
CH2OH
HCO
•C=O
OH•
OH•
e
(Benzyl alcohol)
(Benzaldehyde)
•OC=O
OH•
e, Ar*
CH3•
+
OH
Ring
open
CH3
e, Ar*
(Phenol)
(Benzene)
OH
O
(Benzene, butoxymethyl-)
Ring
open
e, Ar*
OH•
CO2
H2O
H2
CH3
CH3
OH•
OH
(Phenol,3-methyl-)
C≡C
+
CH3
+ CH3•, OH•
HO
C
H2
(1,3-Pentadiene)
(2,4-Hexadien-1-ol)

(a)



(b)

Fig. 7. Possible reaction pathways for toluene destruction initiated by (a) energetic electrons and Ar^*, and (b) OH radicals

4. Conclusion

The effect of Ni/Al_2O_3 catalysts on the plasma-catalytic steam reforming of toluene as a model tar compound was carried out in a DBD plasma reactor. The possible reaction mechanisms and pathways involved in the plasma-catalysis reforming of toluene were proposed and discussed. Compared to the plasma process without catalyst, the coupling of plasma with the Ni catalysts enhanced the conversion of toluene and H_2 yield, whilst

significantly suppressed the formation of undesirable by-products. Increasing the Ni content from 5 wt. % to 20 wt. % considerably enhanced the performance of the hybrid process, which can be attributed to the enhanced catalytic activity due to enhanced dispersion of Ni species on the catalyst surface. These findings suggest that the combination of the plasma with the Ni catalysts shifted the primary reaction pathways of toluene destruction from the dehydrogenation or oxygenation of methyl group to direct cleavage of toluene ring, which can be evidenced by the enhanced yield of hydrogen and C_2H_2.

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